An Introduction of Density Functional Theory and its Application

Di Zhou

This article starts with a brief history and idea interpretation of the Density Functional Theory (DFT), and then explains more detailedly about the original thought of Hohenberg and Kohn and their first and second theorem of the DFT. Next, it also introduces a methodology to treat the calculation based on DFT, which is the Kohn-Sham method based on the Local Density Approximation (LDA) treatment for the exchange energy term. In the later part, this paper touches two examples, as an illustration of how to get the density distribution n(r) from the Hohenberg-Kohn energy F_{HK}, and from this part it shows the derivation in a combination of DFT with the statistical mechanics.

I. What is Density Functional Theory

In 1927, Hartree introduced a procedure to calculate approximate wavefunctions and energies for atoms and ions, and this is called the Hartree function. Some years later, to overcome the totally no-consideration of the anti-symmetry of the electron system, his students Fock and Slater, individually, proposed a self-consistent function with consideration of Pauli principles, and the multi-electron wavefunction in the form of a determinant of one-particle orbitals (Slater-determinant). The calculation of Hartree-Fock model is so complicated, so it was not popular until 1950s. However, the spirit of Hartree-Fock model consider what the result will be get is only an approximation to the real result.

In the same year 1927 as the Hartree function was proposed, Thomas and Fermi proposed a statistical model to compute the energy of atoms by approximate the distribution of electrons in an atom. They expressed the kinetic energy of an atom by the functional of electron density, and add two classic terms of nuclear-electron and electron-electron interactions (both of which can be represented in terms of electron density) to compute the atom energy. At first it didn't contain the exchange energy of an atom, which is a conclusion of Pauli principle and is stated in Hartree-Fock theory, and in 1928 Dirac add an exchange energy functional term[1].

Although the Thomas-Fermi model is an important first step, its applications are very limited currently because it is inaccurate for most of them: the largest source of error is because the representation of the kinetic energy functional term is just an approximation; then the error is in the exchange energy, and is because of the complete neglect of electron correlation effect. But, anyway, it serves as a predecessor of the Density Functional Theory (DFT).

In 1964, Hohenberg and Kohn published a paper, and thus made the foundation of the DFT mansion firm. The core spirit of DFT is to substitute the complicated and thus hard-to-compute many-electron wavefunction, which contains 3N variables (N is the number of electrons, and each electron has 3 spatial variables), with the functional (functional is the function of another function, which map a number to a function) of electron density, which contains only 3 variables. So in the new system, we don't need to be worried about the huge amount of 3N variables, instead, we only deal with 3 variables, which is far easier to handle. Hohenberg and Kohn proposed their first theorem, which points out the ground state energy is uniquely depends on the electron density, which mean it is a functional of electron density. Their second theorem proved that by minimizing the energy of the system according to the electron density, ground state energy can be obtained.

Which must be agreed is that H-K theorems only provide the truth that there exists one-to-one mapping relations between electron density functional and system properties, but they don't give any what exactly these relations are. So what most general used methods, instead of the 'minimizing the system energy', is the Kohn-Sham method. Kohn and Sham published a paper in 1965, only one year later than the publishing of Hohenberg and Kohn's important paper, and in this paper they simplified the multi-electron problem into a problem of non-interaction electrons in an effective potential. This potential includes the external potential and the effects of the Coulomb interactions between the electrons, e.g., the exchange and correlation interactions. Dealing the exchange and correlation interaction is the difficulty within KS-DFT. So far, there still doesn't exist a rigorous way to solve the exchange and correlation energy. However, the simplest approximation is the Local-Density Approximation (LDA). LDA is based upon using the uniform electron gas model to get the exchange energy (which exact value can be get from the Thomas-Fermi model), and to get the correlation energy from fits to the uniform electron gas [1]. By transforming the problem into the non-interacting system in an effective potential, wavefunction can be easily represented by a Slater determinant of orbitals, the kinetic energy functional of this system is exactly known. But the exchange-correlation part of the total energy functional remains unknown.

DFT has become very popular for calculations in solid state physics since 1970s. Compare to other methods dealing with the quantum mechanical multi-body problems, LDA give satisfactory results with experimental data. But in quantum Chemistry area, DFT was still not accurate until 1990s, when the approximation methods were greatly refined to better model the exchange-correlation interaction. DFT is now a leading method for electronic structure calculations in many areas. However, it's still difficult to use DFT to treat the strongly correlated systems, band gap in semiconductors, and strong dispersion systems. So the development of DFT is going on [1].

II. H-K Theorems and K-S Method

1. The First H-K Theorem

Hohenberg and Kohn showed in their first theorem that the ground state properties of a many-electron system are uniquely determined by an electron density that depends on only 3 spatial coordinates (r has 3 variables). They derived their first theorem in the following way: consider a collection of an arbitrary number of electrons, enclosed in a large box and moving under an external potential *v*(r) and the mutual Coulomb repulsion [2]. The Hamiltonian has the form

$$H = T + V + U \tag{1}$$

Where

$$T \equiv \frac{1}{2}\int \nabla\psi^*(r)\int\nabla\psi(r)dr \tag{2}$$

$$V \equiv \int v(r)\psi^*(r)\psi(r)dr \tag{3}$$

$$U = \frac{1}{2}\int\frac{1}{|r-r'|}\psi^*(r)\psi^*(r')\psi(r')\psi(r)drdr' \tag{4}$$

which T is the N-electron kinetic energy, V is the N-electron potential energy from the external field, and U is the electron-electron interaction energy. Here they only deal with the system which ground state is nondegenerate. If there is a magnetic field and thus the states are degenerated, it requires Time Depend DFT to deal with it.

Then note the electron density in the ground state Ψ by

$$n(r) \equiv (\Psi, \psi^*(r)\psi(r)\Psi) \tag{5}$$

Now the logic is: from the expression above, n(r) is clearly a functional of v(r), because wavefunction $\psi(r)$ can be decided by v(r). If it can be proved that v(r) is a unique functional of n(r), and because v(r) can give $\psi(r)$, can fixes H, then if provided n(r), all the properties of ground state are unique functionals of n(r).

Assume another potential v'(r), with ground state Ψ' can give the same density n(r). Ψ' and Ψ can't be equal to each other because they satisfy different Shrödinger equations, so they have different Hamiltonians H and H', and different ground state energies E and E' [2], and they must meet

$$E' = (\Psi', H'\Psi') < (\Psi, H'\Psi) = (\Psi, (H + V' - V)\Psi)$$

so that

$$E' < E + \int [v'(r) - v(r)] n(r) dr \qquad (6)$$

Simply interchange the primed and unprimed quantities and do the same calculation again can get

$$E < E' + \int [v(r) - v'(r)] n(r) dr \qquad (7)$$

add (6) and (7) can get

$$E' + E < E + E' \qquad (8)$$

which can only be true when E=E'. So by this it means there cannot be $v'(r)$ comes from the same n(r), so this proves that $v(r)$ is a unique functional on n(r), and thus proves that the full many-particle ground state is a unique functional of n(r).

2. The Second H-K Theorem

In their second theorem, Hohenberg and Kohn defines an energy functional in terms of the electron density for the system, and further proves that by taking the minimum of the energy functional according to the electron density, ground state energy can be found.

As said above, now all the properties of the ground state are the functionals of electron density, so define

$$F[n(r)] \equiv (\Psi, (T+U)\Psi) \qquad (9)$$

here F[n] is a universal functional and is valid for any number of particles and any external potential (while if it includes V, then it's not universal because V depends on the system)[2]. Then given an external potential v(r), define

$$E_v[n] \equiv \int v(r) n(r) dr + F[n] \qquad (10)$$

for the correct n(r), this is the ground state energy E. Then the logic is, the ground state electron density n(r) will give the minimal value to this functional, and all other electron density will not give the energy larger than the ground state energy.

By doing this, first there should be an restrict condition

$$N[n] \equiv \int n(r) dr = N \qquad (10)$$

This is obviously true because the number of electrons in the system is constant N[2].

From (1), it's easy to get for a system Ψ', the energy functional is

$$\varepsilon_v[\Psi'] \equiv (\Psi', V\Psi') + (\Psi', (T+U)\Psi') \qquad (12)$$

It has a minimum at the correct ground state Ψ, and all other state Ψ' other than the ground state will provide the larger value. Let Ψ' be the ground state of the system with a different external potential v'(r), using (12), and substitute (9) into the later part of (12), can get

$$\varepsilon_v[\Psi'] = \int v(r) n'(r) dr + F[n']$$

$$> \varepsilon_v[\Psi] = \int v(r) n(r) dr + F[n] \qquad (13)$$

remember here Ψ denotes the ground state with external potential v(r), and Ψ' is other state which now is set to represent the ground state with external potential v'(r). And we are only interested in v(r), not v'(r). Now the point is proved.

It's very complicated to find a proper expression of F[n], but once it is found, plugging it into (10), taking the derivative of it to find the minimal value of the functional, and then we get the ground state energy. But usually, the KS-DFT is a better way.

3. Kohn-Sham Method and the Local Density Approximation (LDA)

In another way, (10) can be written into

$$E = \int v(r) n(r) dr + \frac{1}{2} \iint \frac{n(r) n(r')}{|r - r'|} dr dr' + G[n] \qquad (13)$$

where G[n] is a universal functional of the density, and as in section II, this expression is a minimum for the correct density function n(r). G[n] could be written into the sum of two parts

$$G[n] \equiv T_s[n] + E_{xc}[n] \qquad (14)$$

where T_s is the kinetic energy of this noninteracting electrons system, and E_{xc} is the exchange and correlation energy of an interacting system with density n(r). If n(r) is sufficiently slow changing, then

$$E_{xc} = \int n(r)\ \varepsilon_{xc}(n(r))dr \qquad (15)$$

where $\varepsilon_{xc}(n)$ is the exchange and correlation energy per electron of a uniform electron gas with electron density n(r), and here assume $\varepsilon_{xc}(n)$ is known, and it is really can be get from the theories of homogeneous electron gas [3]. Notice this is the LDA, and this quantity is known exactly in the limit of high density and can be computed from the Monte Carlo techniques [3].

Subject to the condition

$$\int \delta n(r)dr = 0 \qquad (16)$$

Can obtain the equation

$$\int \delta n(r)\left\{\varphi(r) + \frac{\delta T_s[n]}{\delta n(r)} + \mu_{xc}(n(r))\right\}dr = 0 \qquad (17)$$

where

$$\varphi(r) = v(r) + \int \frac{n(r')}{|r-r'|}dr' \qquad (18)$$

and

$$\mu_{xc}(n) = d(n\varepsilon_{xc}(n))/dn \qquad (19)$$

is the exchange and correlation chemical energy.

Now we get an effective potential $\varphi(r) + \mu_{xc}(n(r))$ because now the problem comes into an noninteracting electron system moving in the potential $\varphi(r) + \mu_{xc}(n(r))$. Therefore, given φ and μ_{xc}, from solving the one-particle Shrödinger equation

$$\left\{-\frac{1}{2}\nabla^2 + [\varphi(r) + \mu_{xc}(n(r))]\right\}\psi_i(r) = \varepsilon_i\psi_i(r) \qquad (20)$$

After getting the wave equations set, then get n(r)

$$n(r) = \sum_{i=1}^{N} |\psi_i(r)|^2 \qquad (21)$$

From the LDA approximation, very good results are shown. Figure 1 is a solution for an atom of Argon. The shell structure is observed on the plot, which is calculated from the KS-LDA, and the structure is absent from the T-F model. The calculated ground state energy is -19.33eV for KS-LDA and is -24eV for T-F model, while the experimental value is 19.40eV, which is only 0.36% error from the LDA, but is 23.7% from the T-F model[4].

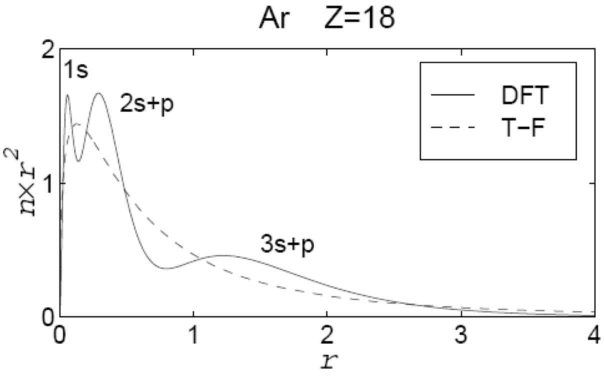

Figure 1[4]

To solve equations (18)-(21) can get the correct n(r), one need to use the self-consistent way: start with an initial guess of n(r), put it into (18) and (19) to get φ and μ_{xc}, use them in (20) to get the eigen wave-functions set and thus get n(r) from (21), then start the whole calculation with the new n(r) again, repeat until convergence is reached [3]. Then, the energy is

$$E = \sum_{i=1}^{N}\varepsilon_i - \frac{1}{2}\iint \frac{n(r)n(r')}{|r-r'|}drdr'$$
$$+\int n(r)[\varepsilon_{xc}(n(r)) - \mu_{xc}(n(r))]dr \qquad (22)$$

the required conditions for this result to be true are slowly varying density or high density.

Following this method, the result of the exact Hydrogen molecule energy, calculated from the Hartree-Fock method, from the LDA method and from the more complicated but accurate General Gradient Approximation (GGA) are plotted. LDA is the simplest possible density functional approximation, and it already greatly improves on Hartree-Fock method. But it just typically overbinds by about 1/20 of a Hartree-Fock method result [5]. The GGA reduces the typical error in LDA by about a factor of 5 (or more).

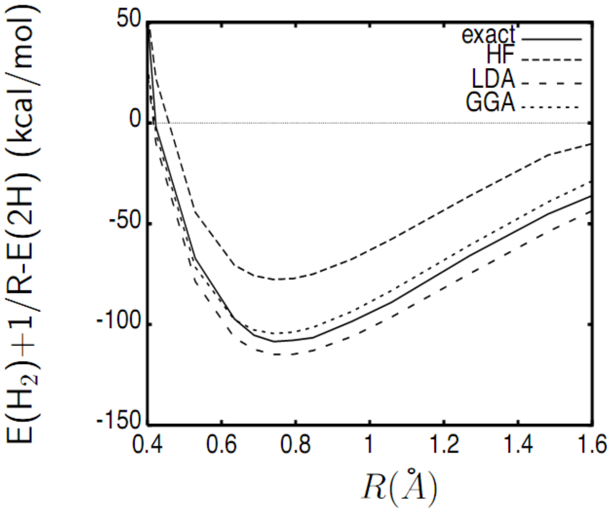

Figure 2[5]

III. Some Examples of the Application of DFT

Here are two examples of finding the expression of electron density by DFT. Here the knowledge of statistical mechanics is also used to help solve the problems. For doing this, we introduce the Hohenberg-Kohn energy $F_{HK}[n(r)]$, which is equal to the internal energy. The existence of F_{HK} is, as discussed above, each system has its unique density distribution n(r). And the effective potential $\varphi(r)+\mu_{xc}(n(r))$ of the system can be obtained from $v(r)=-\dfrac{\delta F_{HK}}{\delta n(r)}$ where v(r) is the effective external potential[4]. Usually the F_{HK} should be written into the sum of a kinetic energy term, a Hartree term, and an exchange-correlation energy term, so its functional derivative of n(r), v(r), should also consists of a effective potential term, a electrostatic potential term, and an exchange-correlation potential, which has been analyzed in previous section.

1. Air

For air, there is no interaction between gas particles, so u(r)=0, so the Hamiltonian (1) now becomes H=T+V. From the statistical mechanics theory, the grand partition function can be expressed as

$$\Xi=\sum_{N=0}^{\infty}\frac{\Xi_1^{\,N}}{N!}=\exp(\Xi_1) \qquad (23)$$

and Ξ_1 is the single particle partition function

$$\Omega=-T\ln\Xi \qquad (24)$$

finish the integral according to p, can get

$$\Xi_1=\int\frac{1}{\lambda^3}\exp\left(\frac{-v(r)}{kT}\right)dr \qquad (25)$$

where λ is a integration constant after the integrating. Again, from statistical mechanics, the grand potential, which now is the free energy

$$\Omega=-T\ln\Xi \qquad (26)$$

now it turns into

$$n(r)\propto\exp(-h/8000) \qquad (27)$$

use the self-consistent method mentioned above, first set

$$n(r)=\lambda^{-3}\exp\left(\frac{-v(r)}{kT}\right) \qquad (28)$$

notice here the density n(r) actually is a initial guess. But now this one is already the correct one, so we should prove it's true. From (28), express v(r) in terms of n(r):

$$v(r)=-kT\ln(n(r)\lambda^3) \qquad (29)$$

and proceeding with the functional Legendre transformation

$$F_{HK}[n(r)]=\Omega[v(r)]-\int n(r)v(r)dr \qquad (30)$$

(here F_{HK} is the Hohenberg-Kohn free energy, it is obtained from a functional Legendre transform) gives

$$F_{HK}[n(r)]=\int n(r)f(n(r),T)dr \qquad (31)$$

where

$$f(n(r),T)=kT(\ln(n\lambda^3)-1) \qquad (32)$$

is the free energy per particle. Then the DFT free energy functional

$$\Omega_v[n(r)]\equiv F_{HK}[n(r)]+\int n(r)v(r)dr \qquad (33)$$

(this is directly derived from the expression of the free energy with the Hohenberg-Kohn free energy) for an ideal air gas is

$$\Omega_v[n(r)] \equiv \int n(r) f(n(r),T)dr + n(r)v(r)dr \text{ .(34)}$$

Minimizing this energy functional with respect to n(r), the left side is zero, and the left side gives

$$v = -\frac{\partial(fn(r))}{\partial n(r)} = -kT\ln(n\lambda^3) \qquad (35)$$

which meets the initial guess (28).

Now we can plug numbers into the express of n(r). The external potential v(r) is $v(r) = mgh - \mu$, where h is the height (set h=0 at Earth's surface, and thus subtract μ at this point), g is 9.8m/s^2, T is about 17^{o}C, m is the mass of a nitrogen molecule which value is about 5*10^{-26} kg. So now $n(r) \propto \exp(-h/8000)$, where 8000 is the length scale[4].

2. Water

Finding the density distribution n(r) of water is more complicated than air, because water molecules have higher density than the air molecules, so the interaction term, u(r), must be taken into consideration. An exact expression of the partition function and its derivative for this situation has not been available yet, so we shall use approximation way to deal with it. Assume the Hohenberg-Kohn energy can still be expressed by (31) as a homogeneous system, although now the system is inhomogeneous. This spirit, as mentioned above, is the LDA. For simplicity, van der Waals model for f(n,T) is used so that both attractive and repulsive interaction of real atoms and molecules are taken into account. Of course some modifications in the previous ideal gas model should be made: add an attractive higher order of n term, representation the attractive force when atoms are away, and subtract from the volume per particle n^{-1} an excluded volume term b, representing the "hard core" of real particles [4]. So now the Helmholtz free-energy per atom in the fluid (32) is:

$$v = -\frac{\partial(nf)}{\partial n} = -kT\left(\frac{b}{n^{-1}-b} + \ln\frac{\lambda^3}{n^{-1}-b}\right) + 2an \qquad (36)$$

and the presser is

$$P = -\left(\frac{\partial F}{\partial V}\right)_N = -\frac{\partial F}{\partial n^{-1}} = \frac{T}{n^{-1}-b} - an^2 \qquad (37).$$

Then solve in the same way as did in the previous part, that is use (34) to get the energy, take the derivative and let the left side be 0 to seek the minimum value extreme condition, and right side turns out to be

$$v = -\frac{\partial(nf)}{\partial n} = -kT\left(\frac{b}{n^{-1}-b} + \ln\frac{\lambda^3}{n^{-1}-b}\right) + 2an \qquad (38).$$

This extreme may have several solutions now, because now several different n(r) could give the same v value. But, the n which gives the lowest free energy is the correct value. In current model, for temperature is not too high and for a limited range of values of v, there are two local minima, corresponding to the liquid and the gas phases of the fluid.

Now again, plug in numbers to discuss the density distribution of water. One earth, in every unit area (per m^2), it is covered by 10^8 moles of water molecule, and each mole has 6.23*10^{23} molecules. The mass is about 0.018 kg/mole, and we choose a as about 0.48Pa*m^6/mole^2 and b as about 1.6*10^{-5}m^3/mole. Use the same expression for the potential $v(r) = mgh - \mu$, and same T and g values as above. Then the final step is inverse (38), express n(r) by v, which step is not available, but only numerically so far. Use T=100^{o}C and P=10^{5}Pa, put them into (37). This is the condition for the boiling water at the surface around the earth, and its numerical solution for n is 56moles/m^3, and is equal to 10^{3}kg/m^3, which really is the density of boiling water [4].

IV. Summary

In the section I, it generally introduce the history of how to solve the multi-electron system wavefunction and energy, from Hartree-Fock approximation to the Density Functional Theory. In the section II, the first and second H-K theorems are briefly explained, and thus lead the discussion of K-S method, which is a feasible way to utilize the H-K model to solve the electrons systems, and also the LDA, which makes the K-S method could be proceeded forth, by dealing the exchange energy part with the uniform gas which can be solved accurately. In section III, there follows two examples, using the Hohenberg-Kohn energy F_{KH}, to try to compute the density distribution of two kinds of big molecule situation in air and water.

Reference

[1] Wikipedia.org, Density Functional Theory term

[2] P. Hohenberg and W. Kohn, '*Inhomogeneous Electron Gas*', Phys. Rev. 136, B 864-871 (1964)

[3] W. Kohn and L. J. Sham, '*Self-Consistent Equations Including Exchange and Correlation Effects*', Phys. Rev. 140, A 1133-1138 (1965)

[4] N. Argaman and G. Makov, '*Density Functional Theory – an introduction*', American Journal of Physics, arXiv.org:physics/9806013 (1999)

[5] K. Burke, '*the ABC of DFT*', (2007)